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Acetals as Possible Diesel Additives

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1. Introduction

Nowadays, oil is the source of the vast majority of fuels used for transport, heating and of the hydrocarbons used in petrochemical industry. However, oil is a fossil fuel and some experts predict that its reserves will exhaust approximately in 20–30 years. Moreover, it seems that the demand of fossil fuels will increase at rates that can be estimated from "World Energy Outlook" elaborated by the International Energy Agency (IEA, 2007). Apart from all these data, there are evidences that the climate of the planet is changing due to the global warning. The temperature of the earth is increasing and the ice of the poles is beginning to melt; all these changes are attributed to the Greenhouse Effect. Besides, it has been estimated that 82 % of the anthropogenic CO_2 emissions are due to fossil fuel combustion so it is clear that alternative energy sources are needed (see Figure 1).

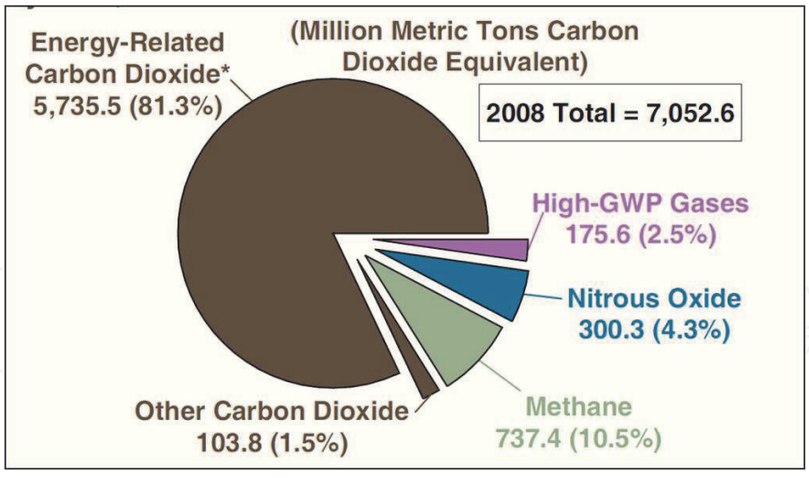

Fig. 1. U.S. Anthropogenic Green house Gas Emissions (IEA, 2008).

On the other hand, the use of other raw materials is being explored due to environmental concerns, economical fluctuations and the geopolitical instability in the producer countries. In order to overcome these difficulties, one possible alternative for transportation is the use of biofuels.

Biodiesel is an alternative fuel obtained from vegetable oils or animal fats and it has several technical advantages over petro-diesel such as the reduction of exhaust emissions, improved

lubricity and biodegradability, higher flash point and lower toxicity. There are some other properties like cetane number, gross heat of combustion and viscosity that are very similar in biodiesels and in conventional diesels. Biodiesels show some worse properties when compared to conventional diesels: oxidation stability, nitrogen oxides emissions, energy content and cold weather operability (Moser et al., 2008). A possible solution to this problem is the use of additives.

A vast variety of fuel additives are added to diesel fuels to improve the engine efficiency and to reduce harmful emissions. An important group of diesel additives are metal-based ones that have been used as combustion catalysts for hydrocarbon fuels. These metals are manganese, iron, copper, barium, cerium, calcium and platinum which present catalytic activity in combustion processes (Burtscher et al., 1999; Keskin et al., 2008). The presence of this type of additives reduces diesel engine pollutant emissions and fuel consumption. The metallic function can react with water to produce hydroxyl radicals, enhancing soot oxidation, or can react directly with the carbon atoms in the soot lowering the emissions (Keskin et al., 2008). However, non-metallic, renewable ashless diesel combustion enhancer additives would be the best option, avoiding the emission of metallic compounds.

Nowadays ethers like MTBE (methyl ter-butyl ether) and ETBE (ethyl ter-butyl ether) are the most well known oxygenated additives for gasoline. ETBE is synthesized by reacting ethanol and isobutylene and it offers better characteristics than the ethanol being less volatile and more miscible with the gasoline.

Ethanol-diesel blend fuel has been studied because ethanol contains 34.3 % of oxygen (Kim & Choi, 2008) so it can reduce the emission of particulate matter (PM) in the diesel engine (Li et al., 2005). Ethanol is an appropriate additive for petrol engines due to its high octane number but due to its low cetane number and its high heat of vaporization it resists self-ignition in diesel engines (Kim & Choi, 2008). Besides that, ethanol – diesel blends are rather unstable even at low temperatures (Frusteri et al., 2007). An alternative to ethanol as oxygenated bio-additives for diesel fuel could be different dieters like acetals (1,1 diethoxy ethane and others). Mention that acetals can be produced from a completely renewable origin.

In the present chapter, a review on acetals will be presented. Its content will include:

- A presentation of different types of acetals (straight chain acetals or cyclic acetals) and their relevant properties.
- A discussion about their different production processes focusing on those processes that have a completely renewable origin.
- The different catalysts used in acetal synthesis, starting from homogenous catalysts to heterogeneous catalyst of various types like commercial or natural ones and also those under development at laboratory scale.
- Finally, an overview of some innovative reaction systems that are currently being tested and developed for this kind of reactions.

2. Acetals formation

Acetals are oxygenated compounds that can be produced following different types of reactions:

- Filley (Filley, 2005) studied the reaction between methyl 9,10 dihydroxystearate and long chain aldehydes to form the corresponding cyclic acetal in the presence of p-toluenesulfonic acid (PTSA).

- Reacting glyoxylic acid with aliphatic alcohols using cationic exchange resins as catalysts (Mahajani, 2000).
- From allylic ethers using as catalysts cobalt compounds (Chang, 1995).
- Reacting aldehydes and ketones with trimethyl/triethyl orthoformate at room temperature in the presence of copper(II) tetrafluoroborate as catalyst (Kumar et al., 2005).
- Reacting ethanol and acetaldehyde in the presence of an acid catalyst. The main reaction implies the production of 1,1 diethoxy ethane and water (Andrade et al., 1986; Capeletti et al., 2000; Chopade et al., 1997a; Chopade et al., 1997b; Kaufhold & El-Chahawi, 1996; Mahajani et al., 1995).

The last procedure is the most interesting one as it is quite a simple reaction and both reactants can have a renewable origin. Ethanol can be obtained via fermentation of sugar rich plants while the aldehyde can be obtained from its corresponding alcohol via partial oxidation or via dehydrogenation so the origin of the acetal can be totally bio/renewable. 1,1 diethoxy ethane has been used as a solvent, as an intermediate in chemical synthesis for the protection of the carbonyl group in ketones and aldehydes, in the fragrance industry as well as in alcoholic drinks like brandy or in several liquors (Capeletti et al. 2000). Moreover, da Silva Ferreira et al. (da Silva Ferreira et al., 2002) and Camara et al. (Camara et al., 2003) studied the presence heterocyclic acetals from glycerol and acetaldehyde in Port and Madeira wines in order to show the existence of a linear correlation between their amounts and the wine age (and its aroma).

One of the first manuscripts on acetalization reactions was published at the end of the 19th century and it is reported by Aksnes et al. (Aksnes et al., 1965). However, all these pioneering works are related to the isolation and identification of the different acetal isomers (Aksnes et al. 1965; Aksnes et al., 1966; Stefanovic et al., 1967).

It must be remarked the important role that glycerol can play in the field of bio-additives. Huge amounts of glycerol are being formed as a subproduct in the *transesterification* reactions of fatty acids (10 wt %). Currently, small amounts of this tri-alcohol are being used in pharmaceutical and personal care areas, so, in order to avoid its incineration, different alternatives are being investigated looking for high added value products from glycerol: hydrogen gas production, glycerin acetate production, citric acid production, cosmetic bonding agent for makeup including eye drops and conversion to propylene glycol, acrolein, ethanol and epichlorhydrin (Silva et al., 2010; Umbarkar et al., 2009). The obtention of glycerol additives would be another interesting use of the glycerol. Thus, it could be a good option to book out all the excedent in glycerol.

Acetal	**Flash point (K)**
Ethanol + acetaldehyde	252.15 ± 0.0
Ethanol + butyraldehyde	302.05 ± 18
Glycerol + formaldehyde	349.35 ± 4.2
Glycerol + butyraldehyde	371.55 ± 23.3
Diesel specifications (EN590:2004)	328.15

Table 2. Flash points of different acetals (Scifinder Scholar 2007 database) and their comparison with the flash point from the diesel specifications (EN590:2004).

However, not all the acetals can be used as diesel or biodiesel additive. Some acetals present low flash points and as a result they are not suitable to use as diesel additives. In Table 1

flash points of several acetals are reported. It can be observed how the glycerol acetals fulfill all the diesel specifications while acetals of ethanol require a big aldehyde in order to get an acceptable flash point. Lower molecular weight acetals are being used as surfactants, flavors, disinfectants (Capeletti et al. 2000; Silva et al. 2010), in cosmetics, food, pharmaceutical area or in fragrances (Umbarkar et al. 2009; Yang et al., 2006).

2.1 Acetals formation from alcohols and aldehydes

The reaction mechanism for straight chain acetals involves two reversible steps. In the first one alcohol molecule reacts with one aldehyde molecule leading to the formation of the corresponding hemiacetal liberating a significant amount of heat. This reaction takes place relatively quickly and in absence of catalyst also at room temperature. In the second step another alcohol molecule reacts with the hydroxyl group of the hemiacetal in order to form the corresponding acetal and water. This second step is also an exothermic reaction but it takes place in presence of an acid catalyst. (Agirre et al., 2010; Chopade & Sharma, 1997a) (see Figure 2).

Acetalization reactions involving polyalcohols (like glycerol) are also carried out in two reversible steps: the first one where the alcohol reacts with the aldehyde molecule leading to the formation of the corresponding hemiacetal and the second one, where two hydroxyl groups of the hemiacetal join to form the corresponding acetal, releasing a water molecule (Chopade & Sharma, 1997b). Silva et al. (da Silva Ferreira et al. 2002) explained in detail the reaction mechanism for the reaction between glycerol and acetaldehyde, indicating all the different steps of the reorganization of the hemiacetal molecule. However, in Figure 3 a simplified scheme of the reaction mechanism proposed by Sharma & Chopade (Chopade & Sharma, 1997b) is shown. It must be mentioned that in the case of reaction between glycerol and acetaldehyde acetals formation was observed in the absence of catalyst although the reaction rate was extremely low.

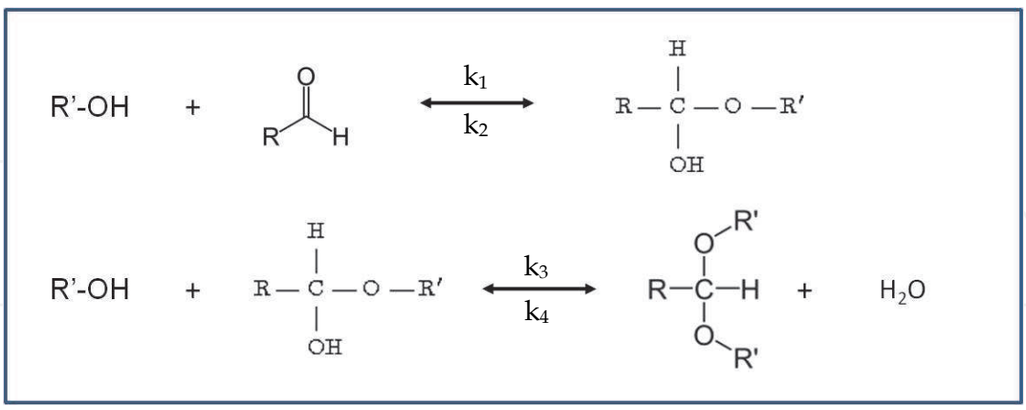

Fig. 2. Mechanism for the formation of straight chain acetals.

In the case of glycerol acetals two different acetals are formed: 1,3 dioxanes and 1,3, dioxalanes. Moreover, each one presents *cis* and *trans* stereoisomers (except when reacting glycerol with formaldehyde) being in the overall four different acetal isomers. Similar to the published results by Camara et al. and Da Silva Ferreira et al. (Camara et al. 2003; da Silva Ferreira et al. 2002), isomerization reaction were observed in our own experiments reacting formaldehyde and acetaldehyde with glycerol, respectively. In all the cases, isomerization of

1,3 dioxalanes to 1,3 dioxanes was observed. Moreover, they observed that 1,3 dioxalane isomers were formed faster but then the reaction mixture proceeded towards the isomerization equilibrium generating more 1,3 dioxanes. On the contrary, Ruiz et al. (Ruiz et al., 2010) observed the isomerization from dioxanes to dioxalanes.

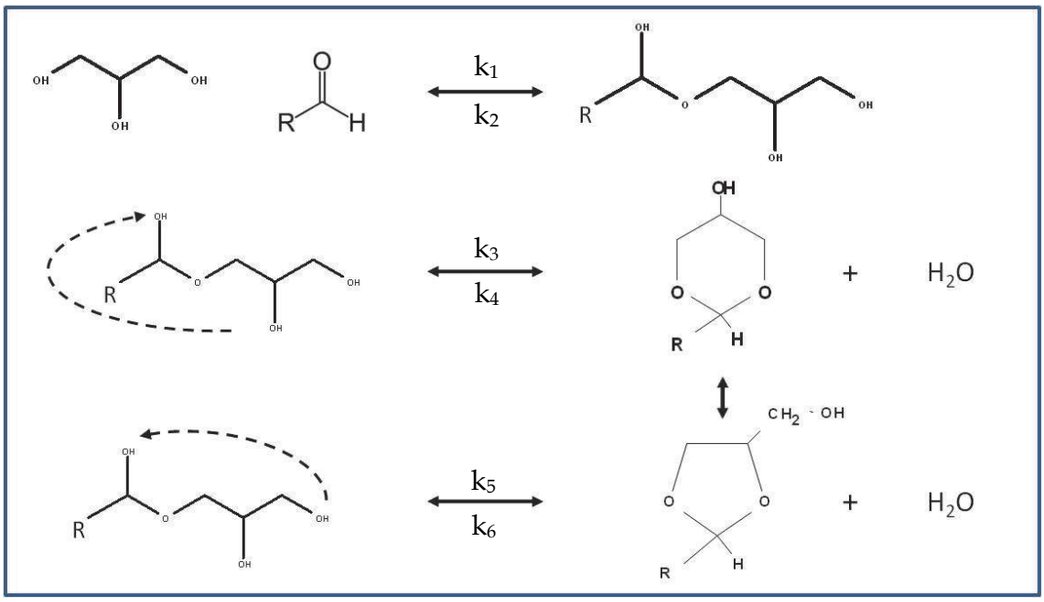

Fig. 3. Mechanism for the formation of cyclic acetals.

2.2 Kinetics of acetals formation reactions

All the information found in the literature shows that this type of reaction presents high thermodynamic limitations. Thus, Sharma and Chopade (Chopade & Sharma, 1997a; Chopade & Sharma, 1997b) achieved a maximum of 50% (at 363 K) of conversion reacting formaldehyde with ethylene glycol and less than 50% (at 343 K) reacting ethanol and formaldehyde. Agirre et al. (Agirre et al., 2010) studied the reaction between ethanol and butanal and the achieved maximum conversion was also around 50% (at 313 K). Other authors like Deutsch et al. (Deutsch et al., 2007) and Silva et al. (Silva et al., 2010) studied glycerol acetalization reactions with different aldehydes. Deutsch et al. (Deutsch et al., 2007) studied the acetalization reaction of glycerol with formaldehyde using different type of solvents and the maximum achieved conversions were between 58-77% (between 313 and 383 K). On the other hand, Silva et al. (Silva et al., 2010) studied the reaction of glycerol with butanal, pentanal, hexanal, octanal and decanal achieving a maximum of 80% (at 343 K) of conversion with butanal. In general, using heavier aldehydes they achieved lower conversions. In all cases thermodynamic limitations seems to be quite important

There are really few publications explaining the kinetics of acetalization reactions in the literature. Only Sharma & Chopade and Agirre et al. (Agirre et al. 2010; Chopade & Sharma, 1997a; Chopade & Sharma, 1997b) have published kinetic information. Thus, they were able to develop a pseudo-homogeneous kinetic model that is able to describe the reaction behaviour according to the reaction mechanism explained in Section 2.1.

It was explained that the hemiacetal formation and decomposition reaction rates are so high at the operating temperatures that the hemiacetal can be considered to be at equilibrium with the alcohol and the aldehyde.

$$[Hemiacetal] = K_1[RHO][R'OH] \quad (1)$$

The formation rate of acetal could be written as

$$\frac{d[Acetal]}{dt} = wk_3[Hemiacetal][R'OH] - wk_4[Aetal][Water] \quad (2)$$

Where w = (g cat)/(reaction volume)
Substituting [Hemiacetal] from Eq. 1,

$$\frac{d[Ac]}{dt} = wk[RHO][R'OH]^2 - wk_4[Acetal][Water] \quad (3)$$

Thus, theoretically it was concluded that the forward reaction is 2nd order with respect to alcohol and 1st order with respect to aldehyde and the reverse reaction is also 1st order with respect to acetal and water, i.e., elemental kinetics. This kinetic expression was confirmed experimentally by the authors in both cases.
Contrary to this behaviour, it was observed that the acetalization reaction between glycerol and acetaldehyde behaves as an irreversible reaction reaching 100% of conversion at different temperatures (Figure 4). In this case the kinetics is only function of the acetaldehyde concentration. The great advantage of this reaction is that, in principle, the industrial production of these acetals to be used as biodiesel additives or for other applications can be carried out in conventional reaction systems.

$$\frac{d[Ac]}{dt} = wk[AcHO] \quad (4)$$

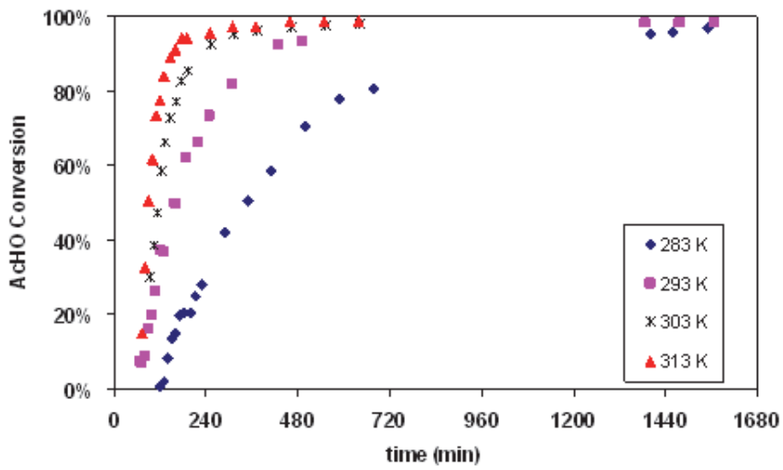

Fig. 4. Effect of the temperature on the acetalization reaction. Batch reactor, (700 rpm, feed ratio 3:1, 2 wt% Amberlyst 47) (Agirre et al. c)

2.3 Solid catalyst for acetal production

Acetals are produced via homogeneous catalytic processes using as catalyst strong mineral acids such as H_2SO_4, HF, HCl or p-toluensuphonic acid (Frusteri et al., 2007; Green, 1981;

Kaufhold & El-Chahawi, 1996). However, these processes entail corrosion problems, are uneconomical and they are not environmentally friendly. The use of a heterogeneous catalytic process would overcome all these problems so, nowadays, several solid acid catalysts are being tested.

One of the first heterogeneous catalytic process for acetal production was described by Andrade et al. (Andrade et al., 1986) in 1986. In this patent an acetal production process from saturated or unsaturated aldehydes and alcohols using strongly acidic ion exchange resins or zeolites is explained. The reaction takes place in the liquid phase and after removal of the catalyst the conversion mixture is extracted by means of water and by means of water insoluble organic solvents. This process is valid for certain alcohols and aldehydes:

An aldehyde of the formula:

$$R_1\text{-CHO}$$

Where R_1 is a straight chain alkyl group having 1 to 3 carbon atoms or alkenyl group with 2 or 3 carbon atoms is reacted with an alcohol of the formula:

$$R_2\text{–OH}$$

In which R_2 is an alkyl group of 1 or 2 carbon atoms.

The method of this invention serves particularly well for the preparation of acetals of the formula:

$$R_1\text{-CH-}(OR_2)_2$$

In terms of catalyst requirement it is recommended to use at least 1.0 g of ion exchange resin and 0.5 g of zeolites per mol of aldehyde used.

In order to find some new active, selective and stable solid acid catalysts for acetal production, Capeletti et al. (Capeletti et al., 2000) reported the performance of several solid acid catalysts of various types, from commercial, natural and laboratory sources shown in Table 2. After characterizing all these catalysts and determining their acidity, their catalytic performances were evaluated by means of experiments reacting ethanol and acetaldehyde. As a conclusion, Capeletti et al. proved that A15 ion exchange resin show better performance than other catalysts reaching equilibrium values much faster than with the others. They also observed that water, a reaction product, seems to have an inhibitory effect on the reaction rate (Capeletti et al., 2000; Mahajani, 2000).

In a review made by Sharma (Sharma, 1995) it is explained how ion-exchange resins, particularly the macroporous variety, are suitable catalysts for oligomerization of olefins, cross-dimerization of olefins, acetalization and ketalization reactions…offering high selectivity rates. Resin catalysts can be used in batch or semi-batch reactors as well as in continuous fixed, expanded or fluidized bed reactors. The heterogenized acidity can exceed the value of 100 % H_2SO_4. In Table 3 Hammett acidity function (H_0) for various acids used as catalysts is shown. More recently (Umbarkar et al., 2009) tested mesoporous MoO_3/SiO_2 solid acid catalyst for glycerol acetalization reaction with different aldehydes showing promising results. On the other hand (Ruiz et al., 2010) tested beta zeolites and Amberlyst resins and they compared them to soluble acids such as p-toluenesulfonic acid (PTSA). They found that in absence of water PTSA and Amberlyst resins are more active but in the presence of water hydrophobic Beta zeolites give better results.

However, acetalization reactions offer really low equilibrium conversions (around 50 % depending on the operating conditions) if they are carried out in a conventional batch

Catalyst	Surface area ($m^2\ g^{-1}$)	Pore vol. ($mL\ g^{-1}$)	Acidity ($meq\ g^{-1}$)
A15. Polystyrene-polydivinylbenzene sulphonic resin, Rohm & Haas	45	0.360	4.7
Acid-treated montmorillonite, Aldrich	345	0.564	0.273
Mordenite, Norton	436	0.210	0.649
Acid treated montmorillonite, natural	235	0.262	0.640
Zeolite FCC cat., Fresh BR1160, Engelhard, UCS: 24.72 Å	342	0.259	0.540
Zeolite FCC catalyst, Isoplus 1000, Engelhard, UCS: 24.40 Å	336	n.a.	0.474
Amorphous FCC catalyst, HA-HPV, Ketjen 25 % Al_2O_3	454	0.688	0.382
Amorphous FCC catalyst, LA-LPV, Ketjen 12 % Al_2O_3	559	0.642	0.350
Equilibrium zeolitic FCC catalyst, BR1160, Engelhard, UCS: 24.31 Å	175	0.213	0.065
Equilibrium zeolitic FCC catalyst, Octavision, FCC S.A., UCS: 24.24 Å	151	0.120	0.160

Table 2. Properties of different types of catalyst reported by (Capeletti M.R. et al. 2000).

reactor (Capeletti et al., 2000; Chopade & Sharma, 1997a; Chopade & Sharma, 1997b; Mahajani et al., 1995; Sharma, 1995). In order to enhance the performance of the acetalization reaction, innovative reaction systems are required. According to the literature reactive distillation processes as well as reactors integrating dehydration membranes seem to be the most promising systems (Benedict et al., 2006; Calvar et al., 2007; Chopade & Sharma, 1997a; Chopade & Sharma, 1997b; Domingues et al., 1999; Feng & Huang, 1996; Lim et al., 2002; Sanz et al., 2006a; Sanz et al., 2006b; Sharma 1995; Zhu et al., 1996).

Acid	**H_0**
p-Toluenesulfonic acid	+0.55
Montmorillonite	
Natural	1.5 to -3.0
Cation exchanged	-5.6 to -8.0
Amberlyst 15	-2.2
Sulfuric acid (40 %)	-2.4
Sulfuric acid (100 %)	-12.3
Nafion	-11 to -13
NY Zeolites	-13.6 to -12.7
$H_3PW_{12}O_4$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (HPA)	-13.16
Lanthanum and cerium exchanged	
HY zeolites	<-14.5
Fluorosulfonic acid	-15.07
Sulfated zirconia	-16
H_3SO_3F-SbF_5	-20

Table 3. Hammett acidity function (H_0) values. (Sharma 1995)

3. Innovative reaction systems for acetalization reactions

As it is explained in sections 2.2 & 2.3 low equilibrium conversions are obtained for acetalization reactions using conventional batch reactors so innovative reaction systems like reactive distillation or reactors integrating dehydration membranes are required in order to achieve high conversions. In these both systems the reaction products, or at least one of the products, are being removed from the reaction shifting the reaction in the forward direction according to Le Chatelier's law.

3.1 Reactive distillation

Reactive distillation (RD) has become an interesting alternative to some conventional processes, especially for those that present high thermodynamic limitations like the acetalization reaction as well as etherification and esterification reactions. RD combines chemical reaction and thermal separation in the same unit. Thus, the reaction products are being removed from the reaction mixture and thermodynamic limitations can be overcome achieving high conversions. The scheme of a typical RD column is shown in Figure 5 Normally, the catalytic section is placed in the middle of the column having two different feed streams, one just above of the catalytic section and the second one just below the catalytic section. However, not always this configuration is the most optimum one.

Sharma and Chopade (Chopade & Sharma, 1997a; Chopade & Sharma, 1997b), Dhale et al. (Dhale et al., 2004) and Agirre et al. (Agirre et al., 2011a) used RD columns for acetalization reactions showing different results.

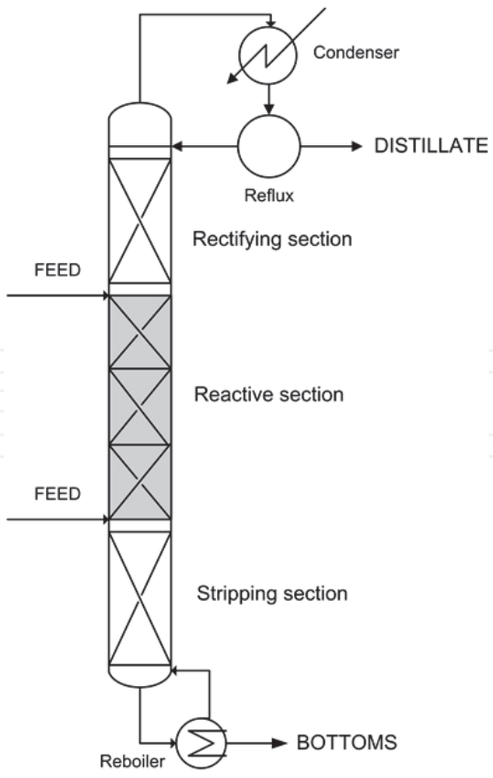

Fig. 5. Schematic diagram of a typical reactive distillation configuration.

Sharma and Chopade studied the reaction between ethanol and ethylen glycol with formaldehyde, respectively. They performed both, batch experiments and RD experiments following the proposed scheme in Figure 5 using two different types of macroporous cation-exchange resins, Indion 130 and Amberlyst 15. Conversions around 45% were achieved in the batch reactor for the first reaction carried out at 333K, 343K and 353K and they observed that the temperature did not have any significant effect on the equilibrium conversion. After that they studied the performance of the reaction in a RD distillation system. Conversions around 86-94% were achieved. At lower reflux ratios higher conversions than operating a high reflux ratios were achieved (at R=0.5 the conversion was 94.0% and at R=4, 86%). In terms of the catalyst the behaviour of Indion 130 and Amberlyst 15 was practically identical.

As indicated, Sharma and Chopade also studied the reaction between ethylene glycol with formaldehyde in a batch reactor and in a RD system. In this case, using an initial feed mol ratio of 1.5:1 ethylen glycol to formaldehyde the final conversion was increased from 42% to 74% using a RD system instead of a conventional batch reactor.

Also Calvar et al. (Calvar et al., 2007) and Klöker et al. (Klöker et al., 2004) showed the benefits of using reactive distillation systems in similar reactions like esterification of acetic acid with ethanol and in the synthesis of ethyl acetate.

In our case, the acetalization reaction between ethanol and butanal was studied. As well as Sharma and Chopade, a previous study was performed in a batch reactor and after that RD experiments were performed. Batch experiments allowed gathering kinetic data of the reaction and also observing the achievable conversions which were between 40% (at 333K) and 50% (293K) (Agirre et al., 2010). Reactive distillation experiments were not as satisfactory as in the previous cases. The maximum achieved conversion was 50% (Agirre et al., 2011a) while at this conditions in a batch reactor the equilibrium conversion would be 39%. Contrary to Sharma and Chopade, increasing the reflux ratio higher conversions were achieved as well as feeding a mixture of both reactants (ethanol and butanal) from the top part of the catalytic section.

All these experiments were performed using Amberlyst 47 ion exchange resin. This resin is equal to Amberlyst 15 resin, the most ussed catalyst in this kind of reactions, but it offers a better mechanical resistance. Another important issue is the way of placement of the resin. Usually the particle size is in the range of 0.5-3 mm so, a simple catalytic bed would offer unacceptable pressure drops. Taylor & Krishna (Taylor & Krishna, 2000) summarizes in a review the most common configurations for the reactive section of a reactive distillation process. The use of structured packing seems to be one of the most suitable options due to its low pressure drop and its high throughput (Klöker et al., 2004). However, when compared to conventional non-reactive structured packings, the specific surface area is moderate. This type of packing presents a really good radial distribution of the liquid phase. Besides, when the catalyst is spent and the columns must be shut down, the packing can be easily removed and replaced by another module. Within the structured packing KATAPAK modules are one of the most common ones.

It can be observed that thermodynamic limitations could be overcome somehow but not significantly. In this case it seems that there are some volatility constraints in order to achieve higher conversions. Taylor and Krishna (Taylor & Krishna, 2000) indicate in an extensive review article the advantages and also the disadvantages or constrains that a reactive distillation systems can offer being one of the constrains the volatility difference between reactants and products.

3.2 Membrane reactors

The use of dehydration membrane reactors is another promising alternative for acetal production. However, no publications were found in this topic apart from the one we published (Agirre et al., 2011b). The continuous water removal from the reaction mixture shifts the reaction to the product side obtaining higher conversions that the achievable ones in conventional reactors.

$$Alcohol + Aldehyde \leftrightarrow Acetal + Water$$

One of the first pervaporation processes studied using a dehydration membrane was the removal of water from ethanol-water mixtures. One of the advantages of doing this separation by using a pervaporation membrane is that complex distillation that is required to break the azeotrope can be avoided. Through the integration of distillation and a membrane step, high separation yields at relatively low capital and operational costs can be achieved (Steinigeweg et al., 2003). In the recent years several dehydration membranes as well as membrane processes for the production of ethers and esters were developed (Lee et al., 2006; Lee et al., 1997; Peters et al., 2007; Sanz & Gmehling, 2006a; Sanz & Gmehling, 2006b).

Sanchez Marcano and Tsotsis (Sanchez Marcano et al., 2002) were among the first to describe the advantages of a membrane reactor for the applications. The continuous removal of water from the reaction mixture through the application of a pervaporation membrane shifts the reaction to the product side and thus increases the yield (Benedict et al., 2003; Domingues et al., 1999; Feng & Huang, 1996; Lim et al., 2002; Sanz & Gmehling, 2006a; Sanz & Gmehling, 2006b; Zhu et al., 1996).

In pervaporation systems, the reaction and the separation can be carried out following different configurations:

1. Passive membrane in recycle loop: it is the most common option. The reaction takes place in a conventional reactor and then the desired or undesired product is separated in a membrane module (Benedict et al., 2003; Benedict et al., 2006; Domingues et al., 1999; Sanz & Gmehling, 2006a; Sanz & Gmehling, 2006b).
2. Passive membrane in reactor: the reaction and separation are carried out in the same unit using non-catalytic membranes and keeping catalyst particles as slurry in the reaction media (Agirre et al. 2011b).
3. Active membrane in reactor: when the reaction and separation takes place in the same unit using catalytically active membranes (Bagnell et al., 1993; Peters et al., 2005; Peters et al. 2007).

With regards to the level of complexity, the first configuration is the simplest one and the last one is the most complex one showing some limitations. On the one hand there is one degree of freedom less than using non-catalytic or inert membranes since the catalyst amount – membrane area ratio uses to be fixed. On the other hand, if the catalyst is deactivated the whole membrane must be replaced and vice versa, if the selective separation layer is damaged for a certain reason it must be replaced including the catalyst. These aspects could represent really big inconveniences at industrial scale. Moreover, due to this complexity, the time to market of catalytically active membranes will be longer than the non-catalytic membrane ones. In terms of the second configuration, passive membranes in reactor, the main issues are to have impact resistant membranes in case of slurry reactors

and the design constraints that the presence of catalyst particles implies in case of multi-tube membranes.

In 1993 Bagnell et al. (Bagnell et al., 1993) studying the esterification of acetic acid with methanol and n-butanol, concluded that catalytically active membranes show higher permselectivities for water at the same or higher flux, compared to when no reaction was taking place within the membrane phase.

In 2005 Peters et al. (Peters et al., 2005) developed a zeolite-coated pervaporation membrane depositing zeolite H-USY layers on a silica membrane by dip-coating using TEOS and Ludox AS-40 as binder material. This membrane was tested in the esterification reaction between acetic acid and butanol. The catalytic activity of the membrane was comparable to the activity of the bulk zeolite catalyst. However, the performance of the system could be improved using a more active catalyst.

On the other hand, other authors have studied pervaporation processes apart from the reaction unit achieving also high efficiencies. Domingues et al. (Domingues et al., 1999) studied the esterification of benzyl alcohol with acetic acid achieving 96 % separation efficiency in water and a reaction conversion of 99 %. Benedict et al. (Benedict et al., 2006) studied the esterification of lactic and succinic acids with ethanol using a pervaporation unit. Removing water from the reaction mixture, they obtained reaction conversions very close to 1. High water fluxes through the membrane were obtained maintaining high recirculation rates and low permeate pressures. Sanz and Gmehling (Sanz & Gmehling, 2006a; Sanz & Gmehling, 2006b) studied the esterification of acetic acid with isopropanol removing the water formed using a pervaporation membrane. Also in this case, conversions above 90 % were achieved.

Another important classification concerns the membrane material, with the two main classes being ceramic and polymeric. In esterification processes, where the pervaporation unit is not integrated in the reaction unit, most of the articles report the use of commercial polymeric dehydration membranes (Benedict et al., 2006; Domingues et al., 1999; Sanz & Gmehling, 2006a; Sanz & Gmehling, 2006b), whereas in those processes where the reaction and the separation are combined in one single reactor polymeric, ceramic and polymeric/ceramic membranes are applied (Bagnell et al., 1993; Bernal et al., 2002; Peters et al., 2005; Peters et al., 2007; Zhu et al., 1996).

As an example, the acetalization of ethanol with butanal was carried out using the second configuration, i.e., placing a passive membrane in a reactor (Agirre et al., 2011b) showing a good behavior. In this work a hybrid silica membrane (HybSi®, developed at ECN) for dehydration was used. This HybSi® membrane has a very high hydrothermal stability and can be used in the dehydration of various organics (ECN, 2010; Castricum et al., 2008a; Castricum et al., 2008b; Castricum et al., 2008c; Kreiter et al., 2009). In the current research the high stability of this membrane under the presence of aggressive organic solvents, like the aldehyde butyraldehyde, and catalyst impacts was confirmed. Thus, by integrating the chemical reaction and the dehydration membrane in one single reactor the equilibrium conversion could be increased from 40% to 70% at 70 ºC (see Figure 6) resulting dehydration membrane reactors more promising than RD systems for the acetalization reaction between ethanol and butanal.

There are not too many publications on the development of continuous membrane reactors. Zhu et al. (Zhu et al., 1996) performed continuous pervaporation experiments in a tubular

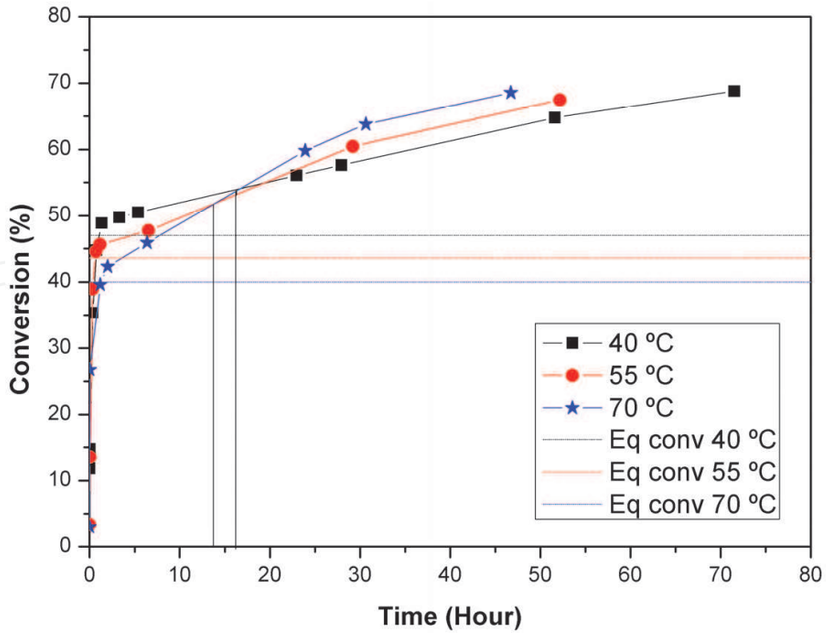

Fig. 6. Effect of the temperature and time on conversion. Conditions: ratio EtOH/Butyraldehyde 2:1 in moles, catalyst loading 0.5 wt%. (Agirre et al. 2011b)

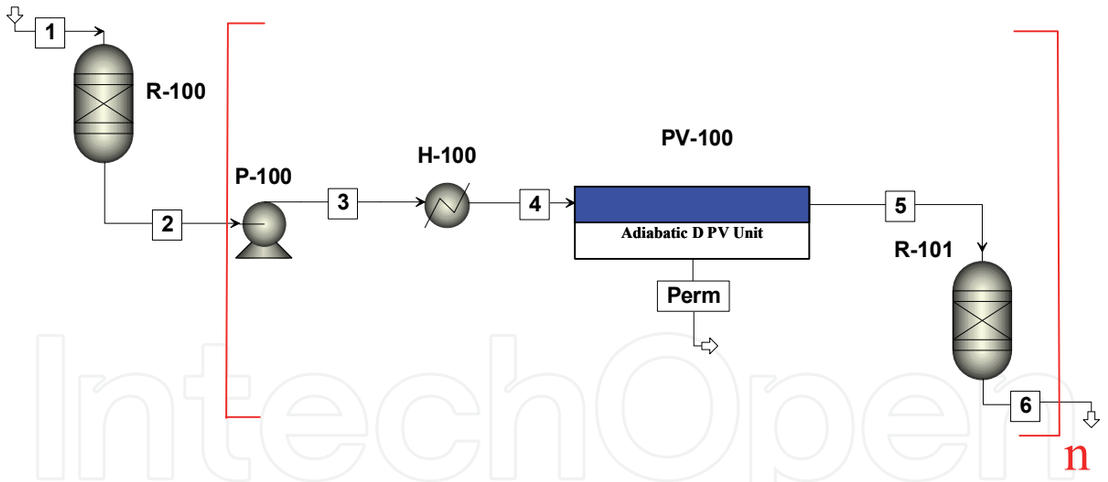

Fig. 7. Flow sheet diagram of PFR and PV modules placed in series.

pervaporation membrane reactor as well as modelling of esterification reactions using H_2SO_4 as homogenous catalyst. De la Iglesia et al. (de la Iglesia et al., 2007) also performed esterification reactions experiments in a continuous tubular reactor. In this case Amberlyst 15 was used as catalyst and it was placed inside the membrane. Lim et al. (Lim et al., 2002) studied different process configurations, and they concluded that tubular membrane reactors lead to a better performance than stirred tank membrane reactors. Nemec et al. (Nemec et al., 2005) analyzed multifunctional tubular reactors with the catalyst particles in the annular region between the membrane and the module shell; their results were not very

satisfactory. In the case study showed in Figure 6 it can be observed that equilibrium conversion is achieved in few hours and then the pervaporation becomes the rate-determining step. Therefore, uncoupled reaction and pervaporation systems seem to be the most promising ones (Figure 7) in order to adjust both the reaction rate and the pervaporation rate.

4. Conclusions

An overview on acetals production has been presented showing different kind of acetals (straight chain and cyclic ones) and different studies in order to choose the most suitable catalyst. On the other hand, due to the high thermodynamic limitations that these reactions show, two different alternative innovative reaction systems have been presented. Depends on the reaction one alternative or the other one (or both) may be more suitable.

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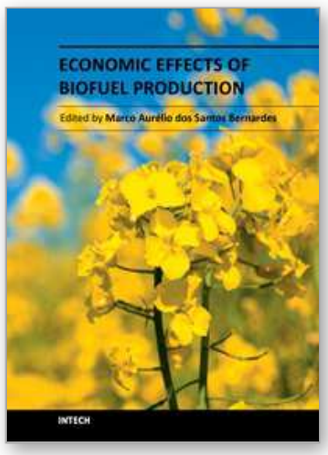

Economic Effects of Biofuel Production

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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